

## Steady State Conduction Current of Doped Polyaniline (PANI) Film Electrets State

DEVENDRA K. SAHU<sup>1</sup>, VIKRAM S. YADAV<sup>2</sup> AMIT K GUPTA<sup>1</sup>,  
SHANKAR LAL<sup>1</sup> and SANTOSH K. SAHU<sup>3</sup>

<sup>1</sup>Department of Physics, R.S. Government Degree College,  
Lalitpur (U.P.)-284 243. India

<sup>3</sup>Neelam College of Engineering & Technology, Agra 284001. India

<sup>2</sup>Department of Applied Science & Humanities,  
Bundelkhand Institute of Engineering & Technology,  
Jhansi (U.P.)-284128. India

### ABSTRACT

The variation of steady state conduction with applied electric field and temperature has been studied in solution-grown hydrochloric acid (HCL) doped Polyaniline (PANI) film 25 $\mu$ m. The study of the steady state conduction current variation with the polymer thickness and with its temperature shows that only the Poole-Frenkel effect can explain the experimental results. Also, hysteresis and polarisation effects were observed in the I-E characteristics. The slope value (m) in the lower field region lies between 1.2 to 1.5 and 1.97 to 2.00 at higher field strength. The activation energy is found to decrease from 0.73eV to 0.65 eV for doped polyaniline as the field increases from 6 to 18 kV/cm.

**Keywords :** Steady State Conduction, Polyaniline (PANI), Poole-Frenkel Effect, Electrets State.

### 1. INTRODUCTION

The electrical conduction in polymeric dielectrics is mainly due to transport of free charge carriers present in the bulk of the conducting polymer and from a number of different conduction processes taking place simultaneously depending upon the experimental conditions. The structure of these materials are sensitive to their electrical, mechanical and thermal history so that the mode of conduction differs from

conducting polymer and the sensitivity of measurement is different for different materials. The electrical conduction phenomena is of considerable significance from two major points of view-firstly, for its own sake, because charge transfer characteristics are of fundamental interest and secondly for the information studies can provide on the nature of electrical contacts which may have a great influence on the measured electrical properties<sup>1</sup>. Steady state conduction in polymers has been extensively studied in the

last decade<sup>2-8</sup> since it provides an understanding of charge carrier, molecular motion, mobility of sub molecules and chemical and physical structure of conducting polymers. It arises due to both electrons and positive ions (mainly protons). The glass transition temperature ( $T_g$ ) is usually the dividing line between protonic (above  $T_g$ ) and electronic (below  $T_g$ ) conductivities. The electrical conductivity in conducting polymers is important due to utility as insulators since dielectric loss is associated with d c conductivity<sup>9</sup>. The dielectric movement of charge carriers has received much attention because of its importance in science and technology which includes leakage current in electrical insulation<sup>10</sup>, charge injection from electrodes which may lead to premature breakdown<sup>11</sup>, various forms of photoconduction and of transient pulse drift and induce conductivity<sup>12</sup>. The steady state conduction provides an understanding of charge carrier transport, molecular motion, mobility of sub molecules and chemical and physical structure of polymers. It arises due to both electrons and positive ions (mainly protons). The glass transition temperature ( $T_g$ ) is usually the dividing the between protonic (above  $T_g$ ) and electronic (below  $T_g$ ) conductivities. Study of d c in polymers becomes important due to their utility as insulators, since dielectric loss is associated with d c conductivity<sup>13</sup>.

The present paper describes the electrical transport phenomena in PANI samples after doping. This study particularly focuses on the electrical properties of doped polyaniline thin film. This is carried out with a view of determining the dominant conduction mechanism.

## 2. EXPERIMENTAL DETAILS

The sample polarization and steady state current measurements have been carried out in a cell using an assembly which is dry, rigid and well established. The cell and assembly have the following properties (i) high insulating resistance (ii) freedom from picking up of spurious potentials and induced charges due to physical motion of the system and (iii) negligible leakage current and less microphonic. To achieve the required degree of precision every consideration of perturbing parameters was taken into account while taking the measurement. All the efforts have been made to minimize the any type of experimental errors. The steady state conduction current was recorded by a 614 Keithley electrometer which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise. The electrometer is specially designed to measure very small direct current, low DC potentials from high impedance source, small charges and high resistance. The field was applied from a high voltage unit EC 4800B. The temperature of the sample was recorded with a calibrated thermocouple attached in close neighbourhood of the sample. The samples thickness was of the order of 25 $\mu$ m.

## 3. RESULTS AND DISCUSSION

The steady state conduction current-field (I-E) characteristics of Hydrochloric (HCL) doped Polyaniline (PANI) films of thickness 25 $\mu$ m at temperature range 40-90<sup>0</sup>C for Al-Al and Al-Cu electrode combination are shown in figure 1 to 2 respectively. Most of the curves show

usually ohmic behavior initially for electric fields below about 20 kV/cm which becomes non ohmic at higher fields. The slope value ( $m$ ) in the lower field region lies between 1.2 to 1.5 and 1.97 to 2.00 at higher field strength.

Figure 3 shows the current-field (I-E) characteristics of doped Polyaniline (PANI) films at different thickness i.e. 25, 40, 50  $\mu\text{m}$  for Al-Al electrode combination. This plot shows that the conduction current is thickness dependent. 25  $\mu\text{m}$  thickness sample exhibits more conduction current than 50  $\mu\text{m}$  thickness of sample. The above results indicate that with the increase of temperature the probability of thermal ionization of the trapping centres increases thus causing a shift in the quasi-Fermi level, which gives rise to a lowering of the barrier across which electrons have to be transported and the conduction becomes more or less ohmic. At lower field, the injection of carriers from contact is less and the initial current is governed by the intrinsic free carriers in the materials. The current will be ohmic until the injected free carrier density becomes comparable with the thermally created carrier density, however at sufficiently higher field; the carriers are mainly due to injected space charges<sup>12-19</sup>.

There are three different types of conduction mechanisms, namely, space charge limited conduction (SCLC)<sup>20</sup>, Schottky-type conduction<sup>18</sup> and Poole-Frenkel conduction mechanism<sup>19</sup>, and one of these mechanisms will be dominant in doped Poly Aniline. According to SCLC theory<sup>20</sup>, the thickness ( $d$ ) dependence of the space charge limited current follows the relation of  $I \propto d^n$ , where  $n$  is a parameter which depends on the trap distribution and is equal

to or greater than three in the presence of traps. Figure 4 shows the dependence of thickness on the current for doped polyaniline films. It is found that the space charge current varies as  $d^{-1.85}$  for doped polyaniline. The value of  $n$  for both polymers is less than that required for space charge limited conduction and so SCLC conduction mechanism is ruled out. A general expression of the current holds equally well for both types (Schottky and Poole-Frenkel) of conduction mechanism is the following form.

$$I = I_0 \exp \left[ \frac{-\vartheta}{kT} + \beta E^{1/2} \right] \quad (1)$$

Where  $\theta$  is the barrier height of electrode-polymer interface,  $T$  is the absolute temperature,  $k$  is the Boltzmann constant,  $E$  is the electric field and the constant  $\beta$  is given by

$$\beta = \left[ \frac{e^3}{a\pi\epsilon\epsilon_0} \right]^{1/2} \quad (2)$$

where the coefficient  $a = 1$  for Poole-Frenkel effect and  $a = 4$  for Schottky emission,  $\epsilon$  is the dielectric constant and  $\epsilon_0$  is the permittivity of free space.

According to Equation (2), a plot of  $\log I$  versus  $E^{1/2}$  should yield a straight line if either of the above mentioned two mechanisms is dominant in HCl doped polyaniline shown in figure 5 (thickness 25  $\mu\text{m}$ ). This further confirms that the conduction mechanism in doped polyaniline thin films is due to either Poole-Frenkel or Schottky. To differentiate between the two conduction mechanisms is to compare the theoretical and experimental values of the  $\beta$

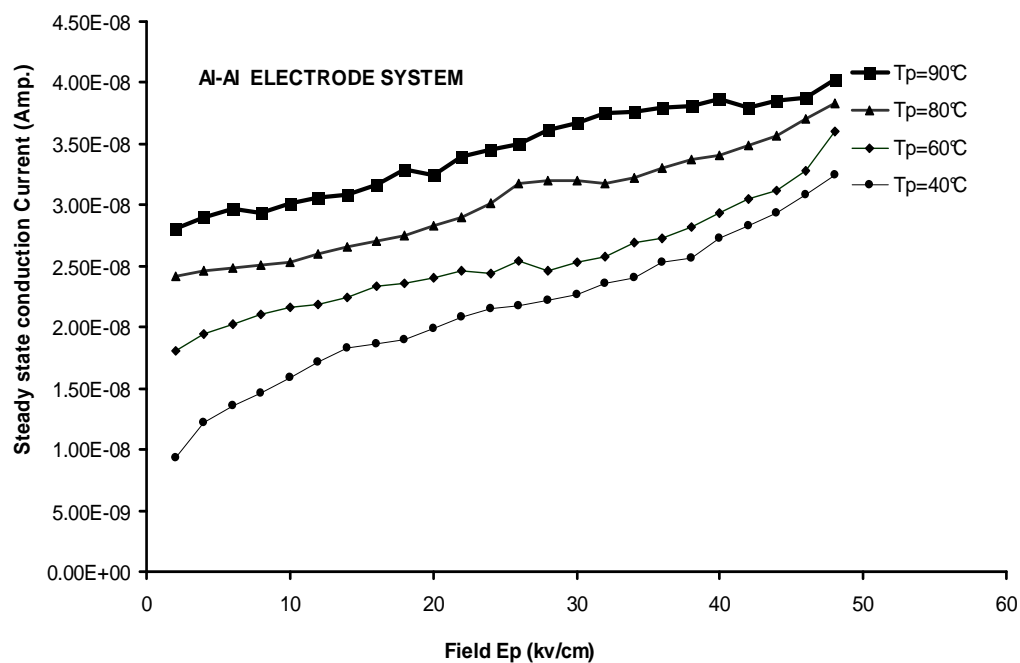
coefficients. The experimental value  $\beta$  ( $\beta_{\text{exp}} = \alpha k T d^{1/2}$ ) is obtained from the slope ( $\alpha$ ) of the linear portion of  $\log I$  versus  $E^{1/2}$  plots for PANI polymers and the theoretical coefficients  $\beta_{\text{RS}}$  &  $\beta_{\text{PF}}$  are calculated by using equation 2. Dielectric constant ( $\epsilon$ ) of doped polyaniline film at high frequency is estimated from the optical transmission studies in the near IR visible region and the value is found. This value of dielectric constant is substituted in equation for PANI polymer to calculate the theoretical  $\beta$  values and is given in (Table 1) along with the experimentally obtained  $\beta$  value. A comparison of the values of the experimental and theoretical  $\beta$  coefficients indicates that in both polymers, the  $\beta$  coefficient value agrees well with the Schottky-type conduction mechanism. However, reports indicate that the mere coincidence of theoretical and experimental  $\beta$  coefficients is not sufficient to establish the dominance of either of the mechanisms<sup>29, 30</sup>. Thus, to confirm the dominance of the Schottky-type conduction mechanism in polyaniline thin films, I-E studies for Al-Cu electrode configurations are also carried out.

From equation 2, it is clear that the current depends exponentially on the barrier height  $\phi_b$ . Thus, in an Al-Cu electrode configuration, the current should also be asymmetric when the bias polarity is reversed. The curve indicates the different directions of the applied field in comparison to Al-Al electrode system for both polymers. The difference between the work functions values of Al-Cu electrode configuration is large enough for both polymers and hence many orders of change should be observed in the conduction current values for opposite directions of the applied field. However, the

difference in the conduction current values for opposite polarities of the applied field in Al-Cu electrode configuration is quite small for both polymers as observed in figure 5. This small difference in the conduction current values may be due to the effects of surface states present at the polymer electrode interface, which can change the potential barrier<sup>31</sup>. The difference in the current values for opposite directions of the applied field though small, can hence be considered as favouring an electrode-dependent Schottky-type conduction in doped polyaniline polymer. The different slopes of the two curves in figure 6 For Schottky-type conduction mechanism, equation 2 requires that the plots of  $\log(I/T^2)$  versus  $(1/T)$  for different values of the applied electric field should be linear. The activation energies can be obtained from the slopes of the linear portions of  $\ln(I/T^2)$  against  $(1/T)$  plots that are shown in figure 7 doped polyaniline of film thickness 25 micron for Al-Al electrode system. As observed in figure 8 the plots yields a straight line, which further confirms that the Schottky-type conduction mechanism is dominant in both polymers<sup>32</sup>. The activation energy is found to decrease from 0.73 eV to 0.65 eV for doped poly aniline as the field increases from 6 to 18 kV/cm. Asymmetric electrode configuration studies show that barrier heights play a significant role in the conduction process. It is found that conduction is an activated process with activation energy decreased as the electric field is increased for poly aniline conducting polymer. From the above observations, it can be inferred that electrode limited Schottky-type conduction is dominant in HCl doped poly aniline thin films.

**Table-1****Theoretical and Experimental value of  $\beta_{RS}$  and  $\beta_{PF}$  for doped Polyaniline (PANI)**

Temp ( $^{\circ}\text{C}$ )	$\beta$ ...X $10^{-5}$	$\beta_{RS}$ (Theo.) ...X $10^{-5}$	$\beta_{PF}$ (Theo.) ...X $10^{-5}$
40	3.21	2.62	5.64
60	3.21	2.59	5.49
80	3.19	2.48	5.32
90	3.18	2.34	5.13

**Fig 1 Current-Field Characteristics of doped PANI thickness 25 micron at different constant temperatures 40,60,80,90°C with Al-Al electrode system**

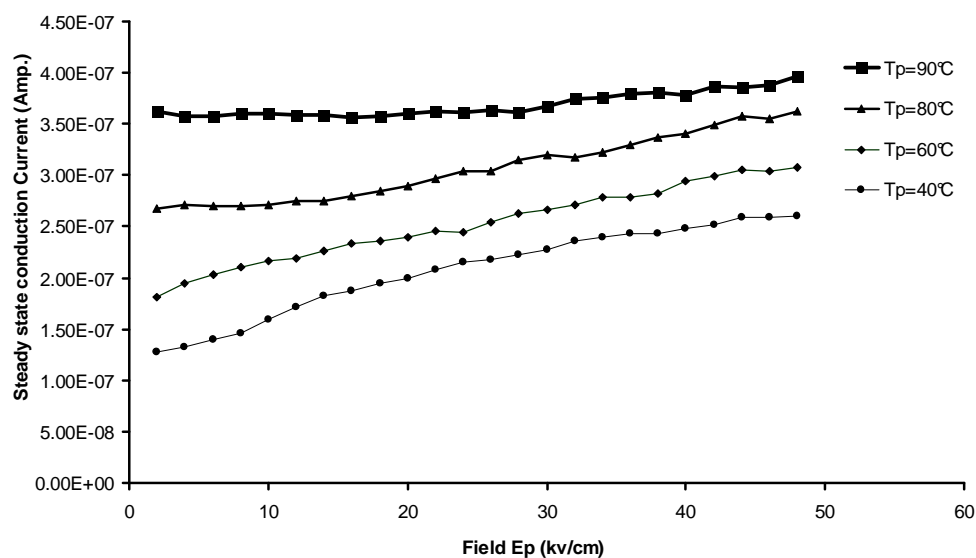


Fig 2 Current-Field Characteristics of doped PMA thickness 25 micron at different constant temperatures 40,60,80 and 90°C with Al-Al system

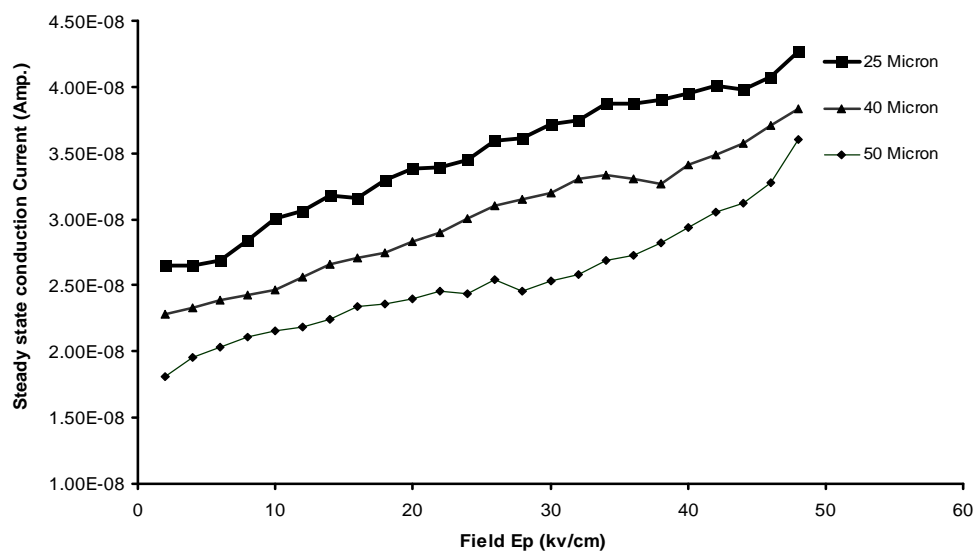


Fig 3 Current-Field Characteristics of doped PANI at constant temperature  $T_p=60^\circ\text{C}$  with different thickness 25,40,50 micron for Al-Al system

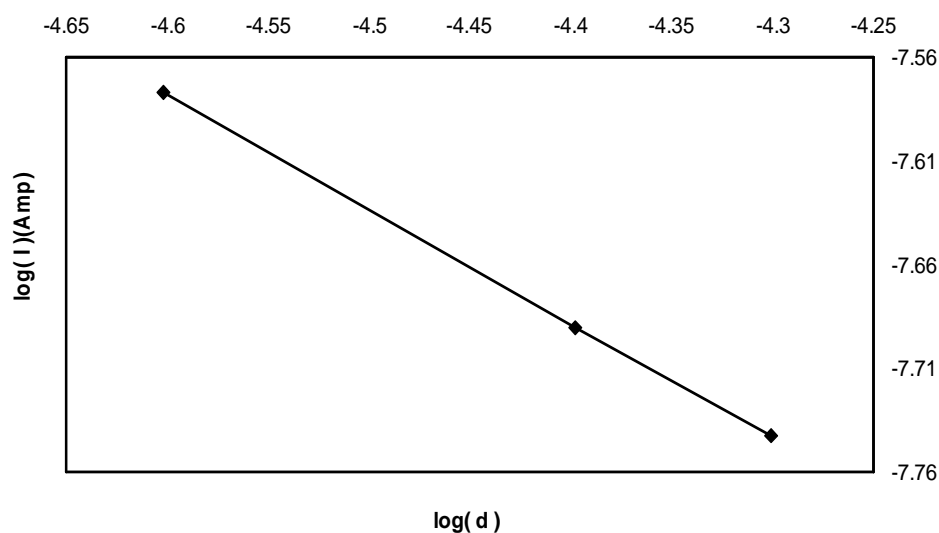


Fig. 4 Thickness dependence on conduction current of doped PANI for Al-Al electrode system

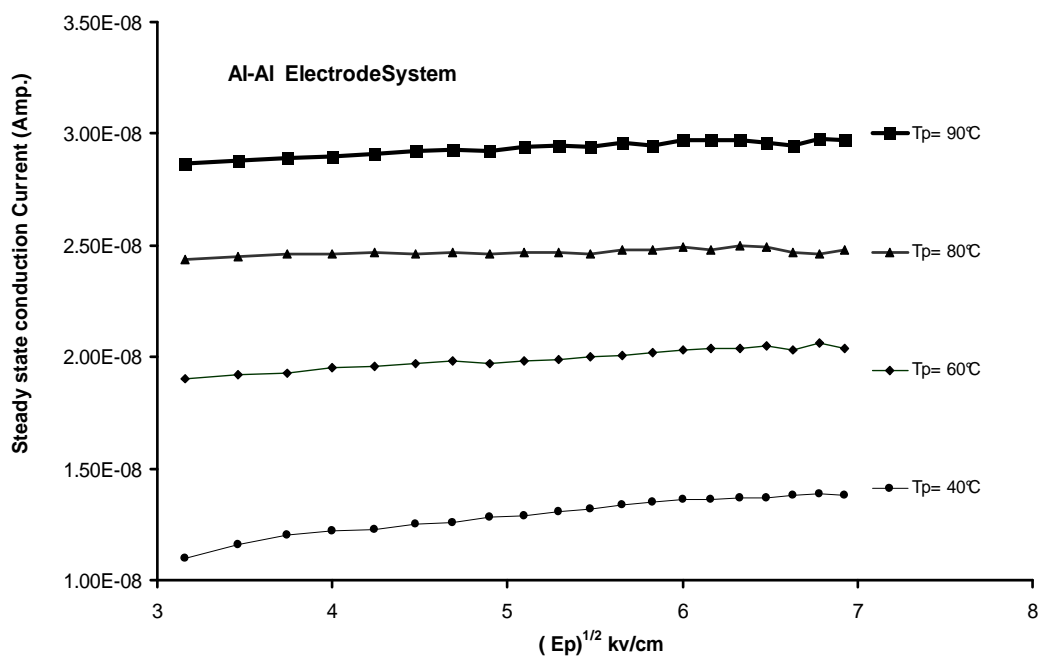


Fig 5 Schottky plots  $\log I$  versus  $E_p^{1/2}$  at various temperatures for doped PANI films of 25 micron thickness for Al-Al electrode system

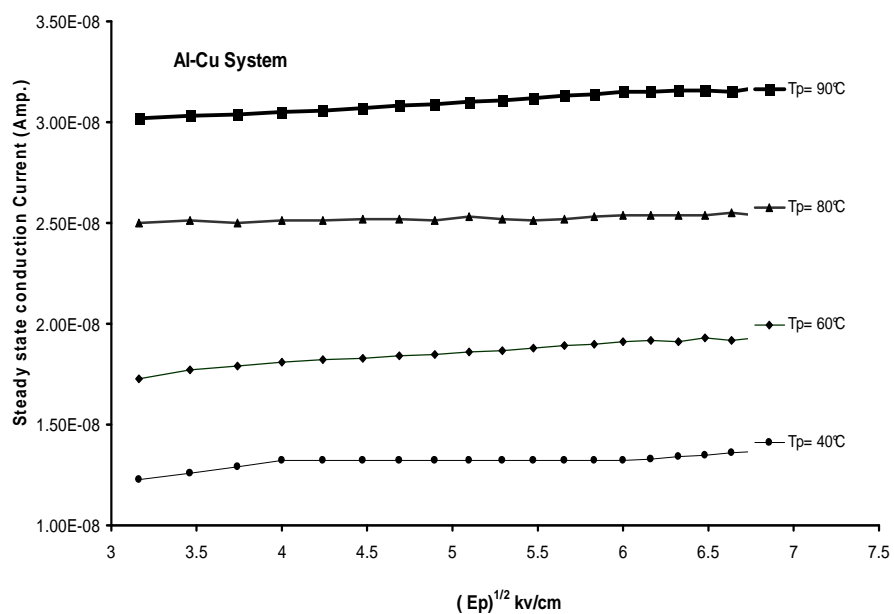


Fig 6 Schottky plots  $\log I$  versus  $E_p^{1/2}$  at various temperatures for doped PANI films of 25 micron thickness for Al-Cu Electrode System

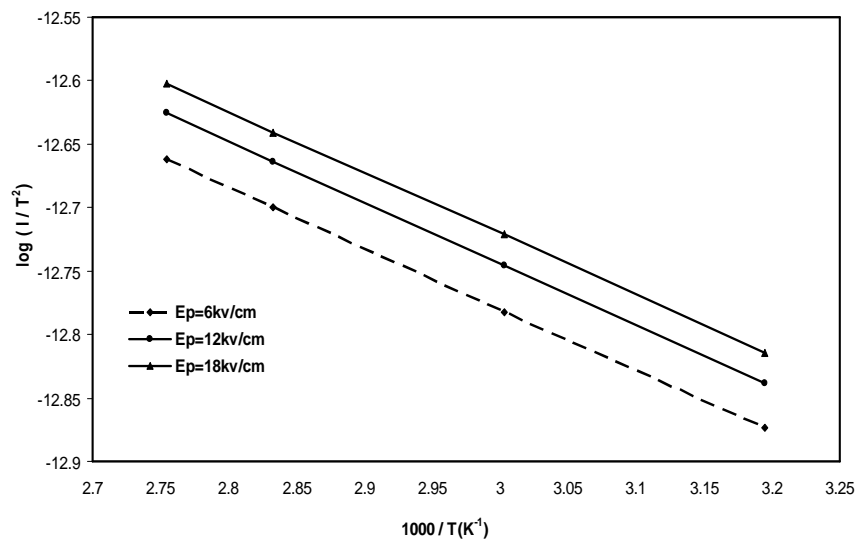


Fig. 7 Plot of  $\log(I/T^2)$  against  $1000/T$  of doped PANI of thickness 25 micron for given electric field for Al-Al electrode system



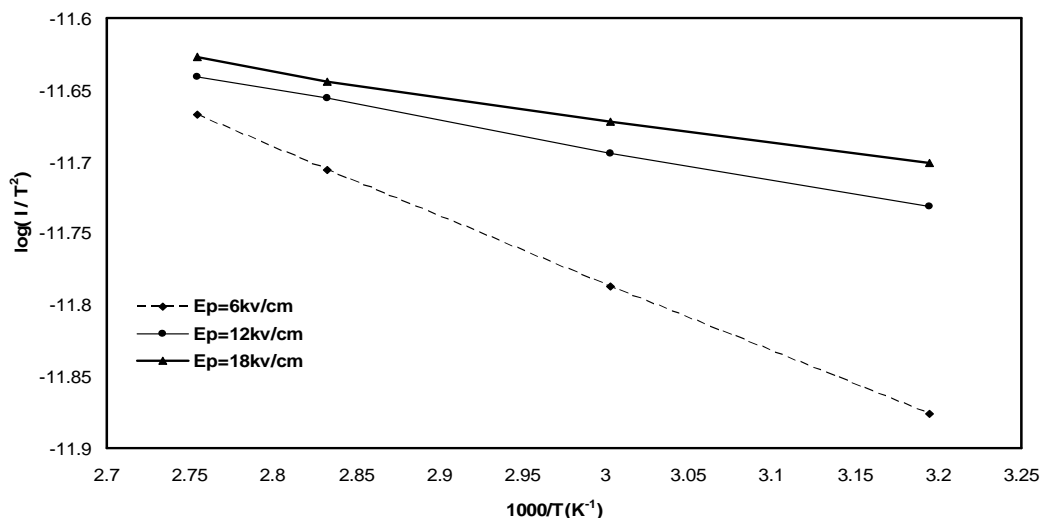


Fig. 8 Plot of  $\log(I/T^2)$  against  $1000/T$  of doped PANI of thickness 25 micron for given electric field for Al-Al electrode system

## REFERENCES

1. P.K. Khare, R.K. Pandey and P.L. Jain, *Indian J. Pure and Appl. Phys.* 23, pp. 325 (2000).
2. K. Laxmi Narayana. Dasardhudu and N. Rao, *Polymer International.* 35, pp. 315 (1994).
3. Ranjeet Singh, P. K. Khare and Reeta Singh, *Indian. J. Phys. A* 71, pp. 39 (1997).
4. P. K. Khare, J. M. Keller, M. S. Gaur and S. C. Datt, *Polymer International.* 35, pp. 337 (1994).
5. J. Keller, S. C. Datt, R. Dubai, R Singh and P. Khare, *Phys. Stat. Solodi.* 139, pp. 391 (1993 ).
6. R. Sahri and H. P. Singh, *Thin Solidfilms.* 69, pp. 281 (1980).
7. A. K. Jonscher and A. A. Ansari, *Phys. Mag.* 23, pp. 205 (1971).
8. Pawan Khare, and A.P.Srivastav, *Indian J. Pure and Appl. Phys.* 29, pp. 410 (1991).
9. P. K. Khare, R. K. Pandey. R. R. Chaurasia and P. L. Jain, *Polymer International.* 49, pp. 719 (2000).
10. M. Taylor and T. J. Lewis, *J. Phys. D,* 4, pp. 1346 (1971).
11. P. K. Khare, J. K. Upadhyay, Ashish Verma and S. K. Paliwal, *Polymer International,* pp. 145 (1998).
12. P. K. Khare and R. S. Chandok, *J. Polym. Mater.* 12, pp. 23 (1995)
13. K. Rangaswami, A. V. Narsimham and J. Sobhanadri, *Indian J. Pure and Appl. Phys.* 33, pp. 279 (1995).
14. H. S. Nalwa, *J. Macromol. Sci. C* 31, pp. 341 (1991).
15. J. Nderherbergh, *ferroelectrics.* 115, pp. 295 (1991).
16. F. Gutman and L.E. Lyons, *Organic Semiconductors* (New York, Wiley 1967).
17. J.G. Simmons, *Phys. Rev. Letts.* 15, pp. 967 (1965).
18. W.Z. Schottky, *Physik.* 15, pp. 872 (1914).

19. Frankel, *J. Phys. Rev.* 97, pp.647 (1938).
20. N.F. Mott and R.W. Gurney, *Electronic Processes in ionic crystals*, Oxford University Press (1948).
21. Rose, *Phys. Rev.* 97, pp.1538 (1955).
22. M. Lampart, *Rep. Prog. Phys.* 27, pp.329 (1964).
23. B.A. Newman, C.H. Yoon, K.D. Pal and J.I. Scheinhein, *J. Appl. Phys.* 50, pp. 6095 (1979).
24. I.S. Zheluder, *Physics of Crystalline Dielectrics*, 2, Plenum Press, New York (1971).
25. H. Akamatu and I. Inokuchi, *J. Chem. Phys.* 18, pp.810 (1950).
26. J.R. Cooper, *J. Phys. Lett.* 36,9, pp. 219 (1975).
27. C.W. Chu, T.H. Gebalk, J.M.E. Harper and R.L. Green, *Phys. Rev. Lett.* 31,25, pp.149 (1973).
28. R.E. Jr. Barker and C.R. Thomas, *J. Appl. Phys.* 35,11, pp.3203 (1964).
29. H. Carchano, M. Valentin, *Thin Solid Films* 30, pp.335 (1975).
30. J. Antula, *Solid-State Electron.* 14, pp. 643 (1971).
31. T. Mizutani, Y. Taki, T. Osawa, M. Ieda, *J. Phys., D. Appl. Phys.* 9, pp. 2253 (1976).
32. D. Sakthi Kumar, *J. Mater. Sci.* 35, pp. 4427 (2000).
33. R.Hasegawa, Y.Takahashi, Y.Chatani and H. Tadokoro, *Polymer International.*, pp. 600 (1972).
34. Devendra. K. Sahu, P .K. Khare and R. K. Srivastava, *Indian J Pure and Appl. Phys.* 43, pp. 207 (2005).
35. P. K. Khare, Ashutosh Verma. Devendra K. Sahu and R. K. Srivastava, *Indian J. Phys.* 77 A (5), pp. 453 (2003).
36. P. K. Khare, Ashish Verma and S. K. Paliwal, *Bull Mater Sci.* 21, pp. 207 (1998).
37. S. Matsumoto, K. Kamisako and K. Shriohara, *J. Appl.Phys.*, pp. 1537 (1976).
38. R. M. Hill, *Philos Mag.*, pp. 2359 (1971).
39. G. Caserta, B. Rispoli and A Serra, *Phys. Stat Sol. A* 35, pp. 237 (1969).
40. N. M. Bashara and C. T. Doty, *J. Appl. Phys.* 35, pp. 3497 (1964).
41. A. Lupu, B. Giuregea and P. Gluck, *J. Polym Sci, Polym Phys.* 12, pp. 2399 (1974).
42. A. K. Jonscher and A. A. Ansari, *Philis Mag.* 23, pp. 205 (1971).
43. P. K. Khare, M. S. Gaur and A. P. Srivastav, *India J. Pure and Appl. Phys.* 32, pp. 14 (1994).
44. M. A. Lampert, *Phys Rev.* 103, pp. 1648 (1995).